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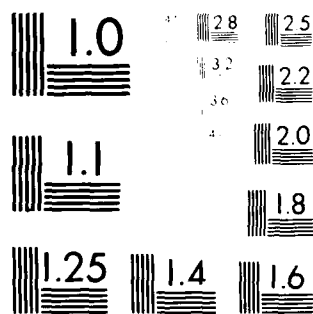   APR 81   A N GENT   N00014-76-C-0408
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THE ROLE OF CHEMICAL BONDING IN THE ADHESION OF ELASTOMERS

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
A review is given of several studies of the effect of interfacial bonding upon the mechanical strength of an adhesive joint. In the first, polybutadiene layers were crosslinked by a free radical process whilst in contact with silane-treated glass. A direct proportionality was found between the minimum peel strength of the joint, as high temperatures and low rates of peeling, and the vinyl content of the silane treatment liquid. Covalent bonding between the diene polymer and vinyl groups on the treated glass was inferred. When radioactively tagged silanes were employed, extensive combination with the

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glass substrates was demonstrated. Again, the greater the amount of vinyl silane found on the treated glass surface, the greater the mechanical strength of adhesion between the treated glass and a polybutadiene overlayer. In another series of experiments two partially-crosslinked sheets of polybutadiene were pressed together before the crosslinking was taken to completion. The additional crosslinking was determined from measurements of the elastic properties and of the degree of equilibrium swelling by a compatible liquid. Again, the mechanical strength of adhesion between the two sheets under threshold conditions was found to be directly proportional to the inferred degree of interfacial interlinking. Thus, at least at high temperatures and low rates of peel, there is substantial evidence for a direct correlation between the mechanical strength of a joint and the degree of interfacial chemical bonding. Moreover, the relationships established in these studies allow other bonding systems to be diagnosed as chemical or physical in nature. For example, a dramatic increase in the strength of adhesion between two crosslinked polybutadiene layers was observed if they were exposed to air or oxygen for periods of an hour or two before being pressed into contact. It is inferred that interfacial chemical bonds are formed as a consequence of rapid surface oxidation reactions.

The Role of Chemical Bonding in the Adhesion of Elastomers

A. N. Gent

Introduction

Although coupling agents are widely employed in
an attempt to form chemical bonds between adherends,
the real nature of the interface and the extent of
chemical coupling achieved is generally rather uncertain.
Indeed, it has been questioned whether interfacial
chemical bonds are formed at all (1). It has been sug-
gested that a strong joint would be developed from
dispersion forces alone (2) and that covalent bonding
at the interface is not really necessary. It has also
been suggested that a high density of interfacial
bonding would be detrimental, making the joint brittle
and weak (3). On the other hand, for adhesive joints
between polymers and metal or glass that are able to
withstand severe conditions of high temperature and
high humidity, it has been found advantageous to employ
coupling agents or adhesion promoters with dual func-
tionality, capable of interlinking the two adherends (4).

Thus, the chemist is presented with a fundamental
dilemma in designing composites:

Is it a good idea to form chemical bonds across
the interface, or is it not?

And if chemical bonding is advantageous, is there
a certain degree of chemical bonding that will confer
maximum strength on the composite?

In view of these fundamental questions, it seemed

worthwhile to carry out a detailed study of the strength
of some model adhesive joints in which the degree of
interfacial bonding could be varied over a wide range
(5 - 8). These studies, carried out over a period of
several years, are the subject of the present review.
As a result of them, it has become clear that chemical
bonding at the interface is, indeed, a strengthening
feature, but that it must take a particular form, using
long extensible molecules as interfacial ties, to be
most effective. Finally, some recent work is described
on interfacial chemical bonds that are formed as a
consequence of surface oxidation reactions in poly-
butadiene (9). This work provides a striking example
that even small amounts of interfacial bonding can
cause dramatic increases in adhesion.

Test Methods for Studying the Adhesion of Elastomers

In order to study the influence of interfacial
bonding on the mechanical strength of an adhesive joint,
it is necessary to minimize all other contributions to
the observed strength. The measured strength of adhesive
joints is larger for ductile, inelastic, and viscoelastic
adhesive materials than it is for purely elastic materials,
because any work expended irreversibly in stressing the
joint up to the point of failure is included in the total
work of detachment. In order to focus attention on inter-

facial bonding, therefore, we must employ purely elastic adherends. We have chosen a model material which comes close to this ideal. It is a simple high-molecular-weight elastomer, polybutadiene, which can be applied to substrates as a thin liquid layer and then lightly crosslinked in situ, to form a soft elastic layer.

After polybutadiene is crosslinked it can no longer undergo liquid-like flow. However, it is still not perfectly elastic because there is a measurable degree of internal friction between molecular segments. This internal friction can be minimized by raising the test temperature, so that molecular Brownian motion is more rapid, and by detaching the adhering layer at very low speeds. Under these conditions, namely at low rates of peeling and at high test temperatures, the adhering polybutadiene layer is almost perfectly elastic.

Moreover, because it is a soft material the tendency to set up interfacial stresses as a result of differential thermal expansion and contraction is quite small. Indeed, in one series of experiments no interfacial stresses at all were set up as a result of thermal expansion or of swelling because the testpiece employed was perfectly symmetrical (8). It consisted of two identical poly-butadiene layers, bonded together, as shown schematically in Figure 1 and discussed in detail later.

In all cases the strength of adhesion was determined

by a peeling experiment, Figures 1 and 2. The work W_a of separation per unit area of interface was calculated from the peel force per unit width of the test specimen,

$$W_a = 2F/w.$$

Bonding Polybutadiene to Glass with Silane Coupling Agents (5 - 7)

The surface density of interfacial chemical bonds between a glass substrate and a lightly-crosslinked layer of polybutadiene elastomer can be varied by first treating the glass with a mixture of vinyl and ethyl silanes (5). It is assumed that vinyl groups added to the glass are capable of bonding to a poly-butadiene layer during a free-radical crosslinking reaction of the latter (Figure 3), whereas the ethyl silane groups are assumed to be quite unreactive towards polybutadiene. In agreement with this assumption, it was found that the resistance to peeling the polybuta-diene layer from the glass substrate increased in direct proportion to the amount of vinyl silane used for treating the glass, Figure 4 (5).

Under near-equilibrium conditions; that is, at low rates of peeling and at high temperatures, the threshold levels of adhesion increased from about 1 J/m^2 for no interfacial covalent bonding, with only ethyl silane groups on the glass surface, to about 40 J/m^2 with all vinyl silane groups on the glass, Figure 4. This large

increase in peel strength is attributed to interfacial
bonding. Direct evidence for the presence of silane
groups on the glass surface has been obtained by radio-
chemical techniques (7), and, again, the greater the
concentration of vinyl silane groups, the stronger was
the elastomer-glass adhesive bond.

The factor of improvement between all ethyl and
all vinyl silane treatments, about 40 times, is com-
parable in size to the relative strengths of covalent
bonds in comparison with dispersion bonds. However,
the absolute magnitudes of the peel strength, both for
no covalent bonding, 1 J/m^2 with ethyl silane, and with
some unknown degree of interfacial bonding, about 40 J/m^2
with vinyl silane, are much greater than can be accounted
for on theoretical grounds, using the surface energies
associated with non-polar dispersion forces and the
dissociation energies for covalent bonds. The discrepancy
is about a factor of 20 in both cases, the measured
threshold strength being about 20 times larger than theory
would predict both for dispersion and covalent bonding.
We attribute this discrepancy to the polymeric character
of the elastomeric adherend: many molecular bonds in a
polymer molecule attached to the substrate must be stressed
before it will become detached (10). Thus, a polymeric
adhesive with long extensible molecules connecting to a
substrate will be much stronger than a rigid or highly-

crosslinked material. In agreement with this hypothesis, the strength of adhesion to glass was found to decrease with increasing crosslinking of the polybutadiene over- layer, as the molecular sequences between points of interlinking were reduced in length and the number of molecular bonds subjected to an equal stress was de- creased (5).

Bonding Polybutadiene to Itself by Free-Radical Cross- linking (8)

The major advantage of the next experimental arrangement is that the density of interlinking between the two components can be inferred with some confidence from the known chemistry of homogeneous crosslinking reactions in elastomers.

The test procedure is as follows: two identical layers of an elastomer are prepared, partially cross- linked ("cured") to the same extent. These layers are then pressed into intimate contact and the crosslinking reaction is taken to completion, Figure 1. By varying the extent of crosslinking before the layers are brought into contact, the degree of chemical interlinking can be varied over the entire range, from zero, when two fully- cured sheets were pressed together, up to a level characteristic of the density of crosslinking within a fully-cured sheet when the layers are brought together before any crosslinking takes place. Moreover, the

density of crosslinking within simple elastomer systems
can be determined at various stages in the crosslinking
process. We have employed measurements of elastic
behavior and equilibrium swelling in n-heptane to
provide estimates of the degree of crosslinking at
various times of reaction and hence of the degree of
interlinking when two sheets are brought together after
partial crosslinking and then the crosslinking reaction
is taken to completion.

Again, the test material used in these experiments
was polybutadiene, and for the same reasons as before.
It is relatively pure, non-polar and non-crystallizing.
It crosslinks readily by a free-radical mechanism, with
small amounts of dicumyl peroxide. It has an extremely
low glass transition temperature of about -95^0C and
hence experiments can be carried out under near-equilib-
rium conditions at moderate temperatures.

Because the two-layer testpiece is symmetrical, no
shrinkage stresses are developed on warming or cooling.
Furthermore, the testpiece could be swollen uniformly
by compatible liquids so that the dissipative properties
of the elastomer were reduced still further, without
introducing stresses at the interface. Thus, measurements
of the mechanical strength could be made using swollen
testpieces to test the hypothesis that a constant low
value is attained in the absence of mechanical energy

dissipation within the adherends, and that it is this threshold value which is directly related to the degree of interfacial bonding.

Measurements of the strength of adhesion are shown in Figure 5 where the work W_a of detachment is plotted against the rate R of peeling. These measurements were carried out at a temperature of $100^\circ C$ to minimize visco-elastic contributions to the observed peel strength. At the lowest rates of peeling the results do, indeed, approach asymptotically towards threshold values, which range from 5 to 60 J/m^2, depending upon the degree of chemical interlinking. Moreover, the same minimum values were obtained with swollen test pieces, denoted by open circles in Figure 5, when allowance was made for the reduced density of molecular strands in the swollen material by the areal factor λ_s^2, where λ_s is the linear swelling ratio. In these experiments the time t_1 of crosslinking the two sheets separately before they were brought together for subsequent reaction for a further time t_2 was varied from 0 to 90 minutes. The sheets were fully crosslinked after 90 minutes and,therefore, the lowest curves in Figure 5 represent adhesion with little or no chemical interlinking. On the other hand, the uppermost curves represent zero time of crosslinking of the sheets separately, and full crosslinking together. in this case, the interlinking takes place to the same

extent as the crosslinking within each sheet so that they become fused into one homogeneous sheet and the peeling experiment consists of tearing through a single block.

In Figure 6, values of the detachment energy W_a determined under threshold conditions, obtained by extrapolating experimental values over a wide range of peel velocities to a zero-velocity condition, are plotted against the increase $\Delta\nu$ in the density of network strands due to further crosslinking whilst the sheets were in contact. $\Delta\nu$ is employed as a measure of the amount of interlinking. It was determined by means of the Flory-Huggins theoretical relation between equilibrium swelling and density ν of network strands in a crosslinked elastomer (11). As can be seen, the threshold strength of adhesion was found to increase in direct proportion to the degree of interfacial bonding, from very low values up to the measured cohesive tear strength, denoted by open circles for the two levels of crosslinking employed in these experiments. Thus, there appears to be a direct proportionality between the mechanical strength obtained under threshold conditions and the density of chemical bonding between the two elastomer layers.

It is noteworthy that the sheets prepared with 0.2 percent dicumyl peroxide crosslinking agent were weaker under all circumstances than the sheets prepared with a smaller amount of dicumyl peroxide. They were weaker in

adhesion and weaker in cohesion, in the fully-reacted state. This observation again points to the importance of the length of the molecular sequences composing an adhesive. When the molecular ties are long, they contain a large number of bonds, all of which must be stressed highly in order to break one of them. When the material is highly crosslinked and the molecular sequences are short, then it is both less extensible and weaker.

Bonding Polybutadiene to Itself by Surface Oxidation Reactions (9)

An unusual bonding process has recently been encountered. Extremely strong bonding has been observed between some fully-crosslinked polybutadiene sheets when they were exposed to air for short periods at room temperature before being pressed together. In some cases the two sheets could not later be separated. The experiments were carried out as follows.

Thin sheets were prepared between layers of a polyester film (Mylar film, from E. I. duPont de Nemours and Co.). The Mylar film was then removed from each of the two sheets, exposing the elastomer surfaces to air. After a given period of time two elastomer surfaces were brought into contact and pressed together under a light force for a further period, generally 24 hours, at room temperature. This procedure is shown schematically in Figure 7. The strength of adhesion was then measured by

peeling the adhering strips apart.

All of these peel tests were carried out at room temperature and at a peel rate of 80 μm/s. These conditions are not sufficiently gentle to eliminate visco-elastic contributions to the work of detachment altogether. Only a qualitative interpretation of the experimental results is, therefore, attempted.

As shown in Figure 8, the strength of self-adhesion of crosslinked strips of polybutadiene depended strongly upon the period of exposure to air before they were brought into contact. Initially rather low, the peel strength rose dramatically as the period of exposure to air increased, so that after exposure for 1-2 hours before the strips were pressed together, they could not be separated without tearing the elastomer layers. For exposure periods greater than about 2 hours the subsequent adhesion became weaker, and it fell rapidly as the exposure time was increased still further. Eventually, after exposure periods of about 10 days, the self-adhesion of the elastomer layers was quite small, comparable to the initial value.

If the protective Mylar films were removed from the elastomer layers in an atmosphere of nitrogen (in a glove box) and the two layers were then pressed together, the resulting strength of adhesion was found to be low and

constant, independent of the period which elapsed between removing the Mylar films and joining the elastomer layers together, Figure 8. Thus, the striking increases, and later decreases, in adhesion shown in the Figure appear to be a result of reaction of polybutadiene with atmospheric oxygen.

In striking contrast to the strong adhesion developed in polybutadiene materials, no comparable effect was observed with natural or synthetic cis-polyisoprene. Indeed, the self-adhesion of crosslinked layers of natural rubber was found to be decreased somewhat by prior exposure to air. Now, it is well-known that oxidative reactions lead to further crosslinking and hardening of polybutadiene vulcanizates whereas, in contrast, they generally lead to softening of polyisoprene vulcanizates as a result of molecular scission (12). Thus, the observed adhesion phenomenon is wholly consistent with the development of interfacial bonding by means of oxidative processes in those polymers for which molecular interlinking is the principal result of oxidation.

Oxidation of polyolefins is reported to involve two main propagation steps (12):

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$RO_2\cdot + R'H \longrightarrow RO_2H + R'\cdot$$
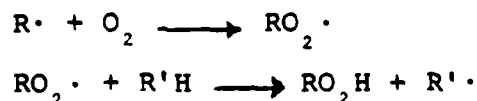
In the first, a polymer radical reacts with oxygen to form
the peroxy radical which, in the second step, abstracts
H from a nearby group to form a hydroperoxide and a second
radical. Moreover, the hydroperoxide itself decomposes
slowly, generating further radical species, so that the
process is autocatalytic.

Now, this general reaction scheme does not account
for crosslinking and hardening during oxidation. Another
reaction must therefore be invoked: the addition of
polymer radicals to other polymer molecules to form
intermolecular bonds.

$$R\cdot + R' \longrightarrow RR'\cdot$$

This reaction is known to occur in polybutadiene
by addition to the C-C double bond but not to a signif-
icant degree in polyisoprene where the radicals appear
to be less reactive. Thus, it can account for the
interfacial bonding observed with polybutadiene but not
with polyisoprene. Moreover, it will become proportion-
ately greater in importance as the concentration of
oxygen becomes lower, i.e., as oxidation continues in
the interfacial region after the elastomer layers have
been brought into contact. We therefore infer that
this radical addition is responsible for the observed
adhesion.

Conclusions

Chemical interlinking between two layers of a model elastomer, or between a layer of elastomer and a rigid glass substrate, has been shown to cause large increases in the strength of adhesion. Indeed, the increase in peel strength appears to be approximately proportional to the density of interfacial bonds.

There are three other aspects of this correlation that must be mentioned, however. First, it is most clearly seen under threshold conditions when other contributions to the measured strength arising from internal dissipation processes (viscous processes, ductile flow, plastic yielding, internal cavitation, detachment from filler particles, etc.) are all absent. The effect of interfacial bonding is not so obvious when these other processes are present because they can raise the observed strength of adhesion by as much as 3 or 4 orders of magnitude (13-16).

Secondly, the absolute values of the strength of adhesion, even under theshold conditions, are much larger than simple thermodynamic calculations would suggest. This discrepancy, by a factor of about 20 in our experiments, is attributed to the Lake-Thomas mechanism (10): many molecular bonds must be stressed in order to break or detach a single molecular chain

in an elastomeric network.   In consequence, the greater
the degree of   internal crosslinking,
the weaker the adhesive joint.

Finally, attention has been drawn to an example
of inadvertent interlinking, when materials capable of
free-radical crosslinking are brought into contact
after surface oxidation has started.   It is remarkable
that strong bonding is obtained when the oxidation
process is at an early stage and reveals again that a
small number of long, extensible, interlinking molecules
can produce strong adhesive joints.

Acknowledgements

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Figure Legends

1. (Symmetrical Test Method.)

2. Test method for adhesion of an elastomer layer to
    glass.

3. Bonding polybutadiene (PB) to glass treated with a
    mixture of vinylsilane (R) and ethylsilane (R').
    The elastomer layer is crosslinked and interlinked
    in situ by a free-radical-producing agent, dicumyl
    peroxide (DCP).

4. Threshold work of detachment W_o for polybutadiene vs
    the fraction of vinylsilane in the mixture of vinyl
    and ethyl silanes used to treat a glass surface.
    Taken from reference 5.

5. Work of detachment W_a vs the rate R of peeling for
    partially-interlinked sheets of polybutadiene (PB),
    dry (●) and swollen with paraffin oil (0). Taken
    from reference 8.

6. Threshold work of detachment W_o vs the degree of inter-
    linking $\Delta\nu$ between two sheets of polybutadiene. Taken
    from reference 8.

7. Interlinking between two sheets of polybutadiene as a
    result of prior exposure to air.

8. Work of detachment W_a vs the time of exposure to air
    or nitrogen before the two sheets of polybutadiene
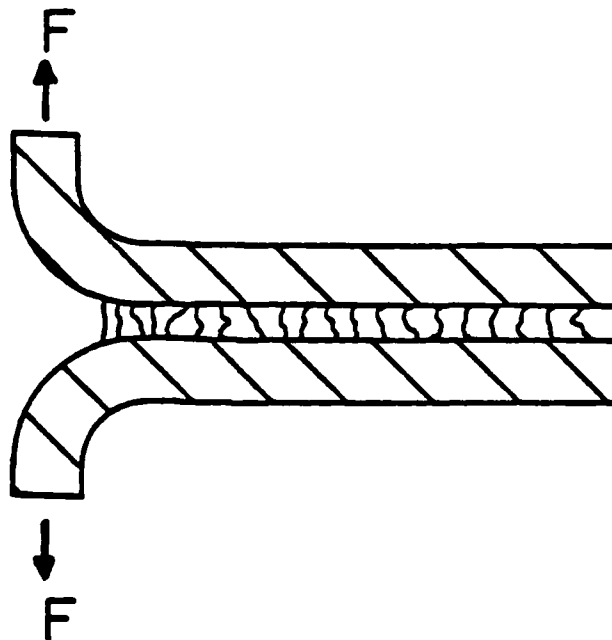   were pressed together. Taken from reference 9.
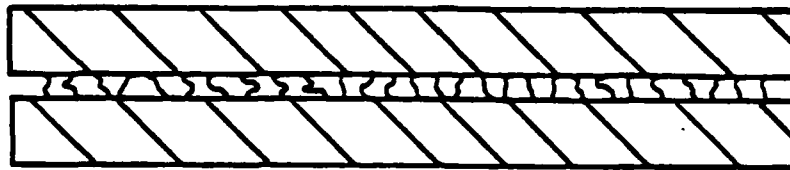
Symmetrical test method

FIGURE 1

$$W_a = 2F/w$$

FIGURE 2

Cloth

PB + DCP

R — R

R' — R

GLASS

R : Vinyl
R': Ethyl

150°C
2hrs

Cloth

CROSSLINKED PB

R'

GLASS

Adhesion with Chemical
Bond
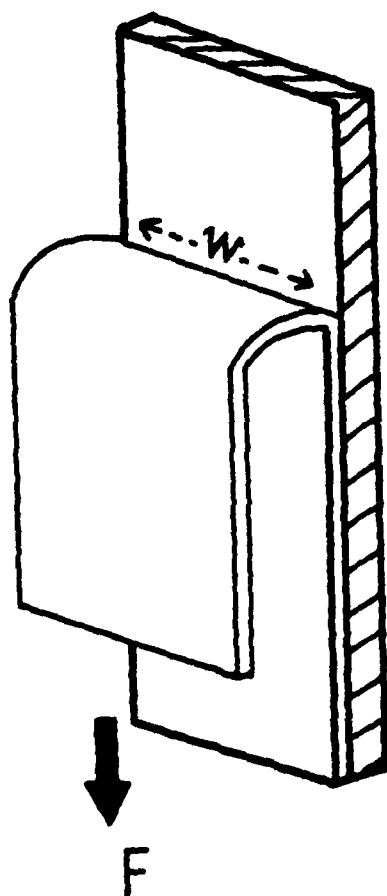
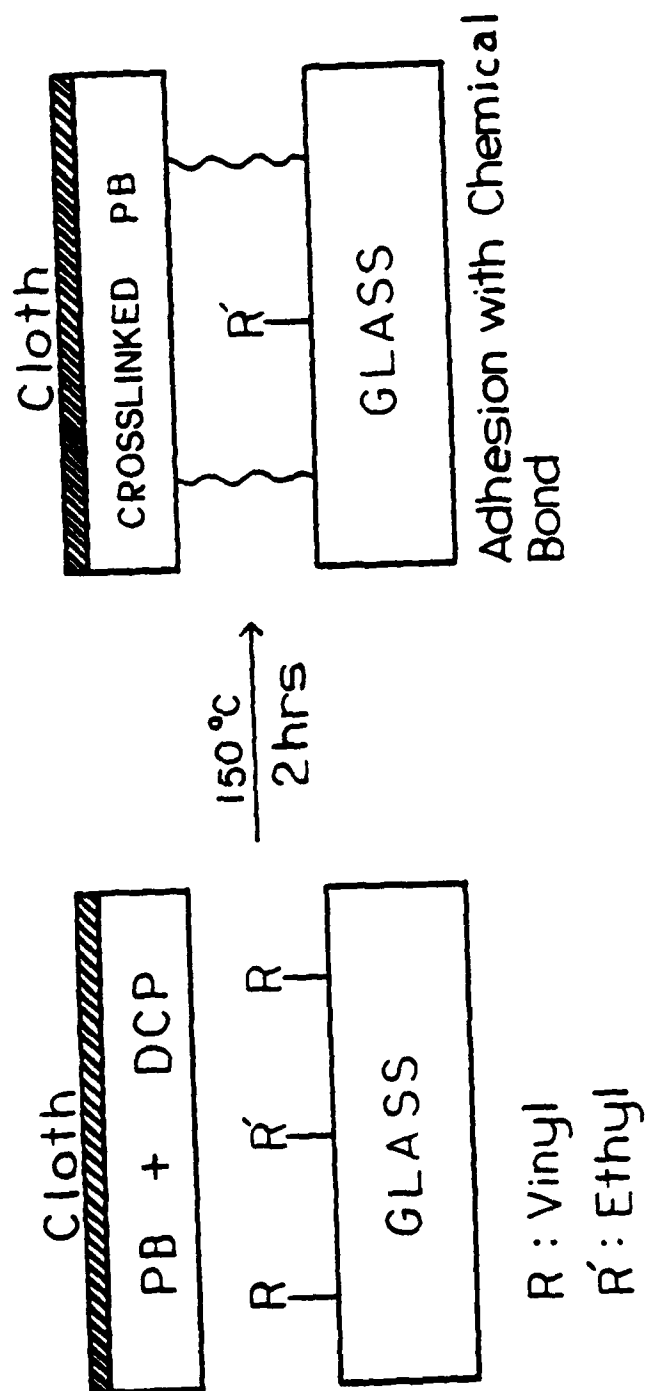FIGURE 3

Threshold adhesion W_0 vs. vinyl silane fraction on glass

FIGURE 4

Work of separation W_a for PB layers

FIGURE 5

Work of separation W_o vs. $\Delta \nu$
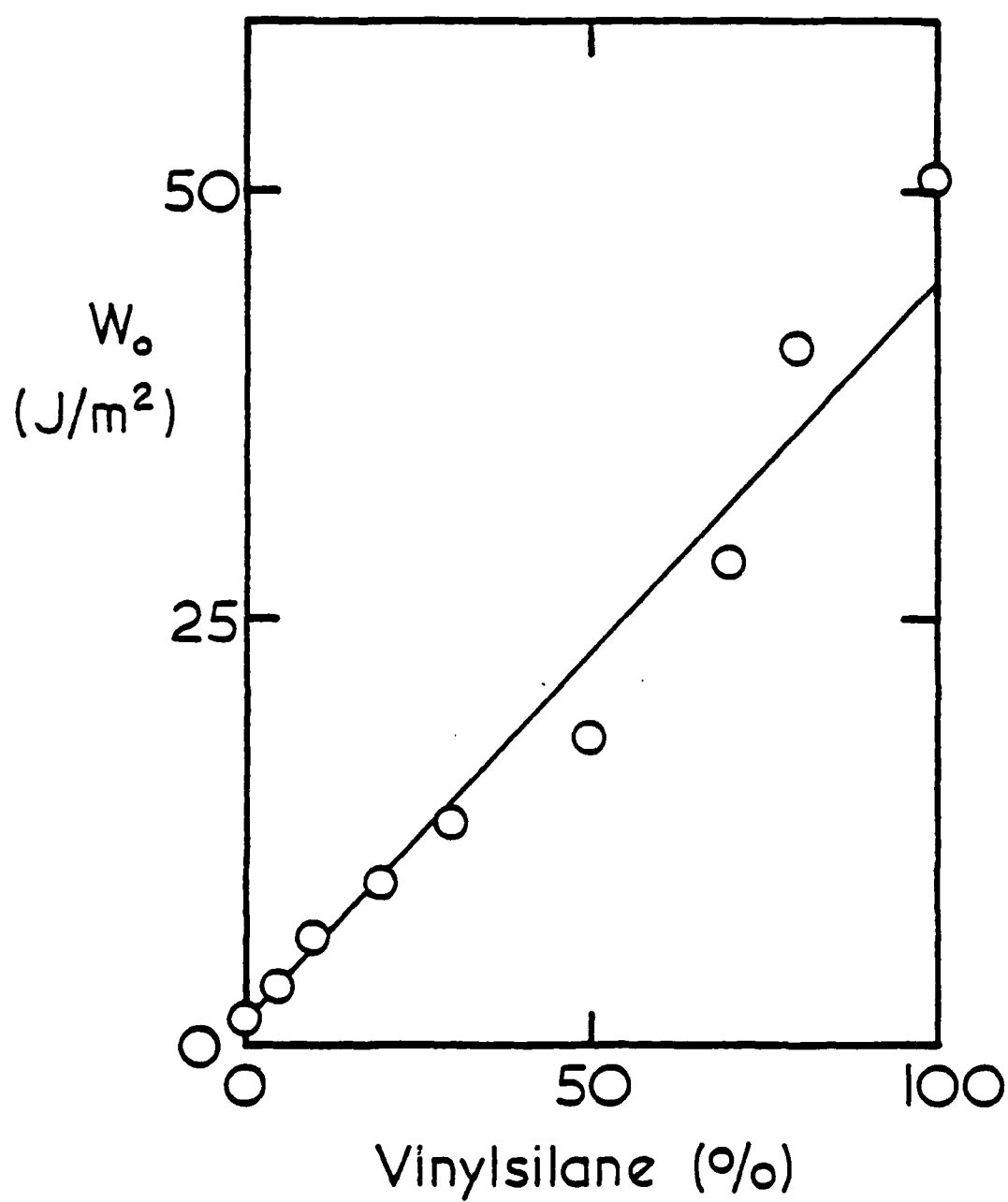
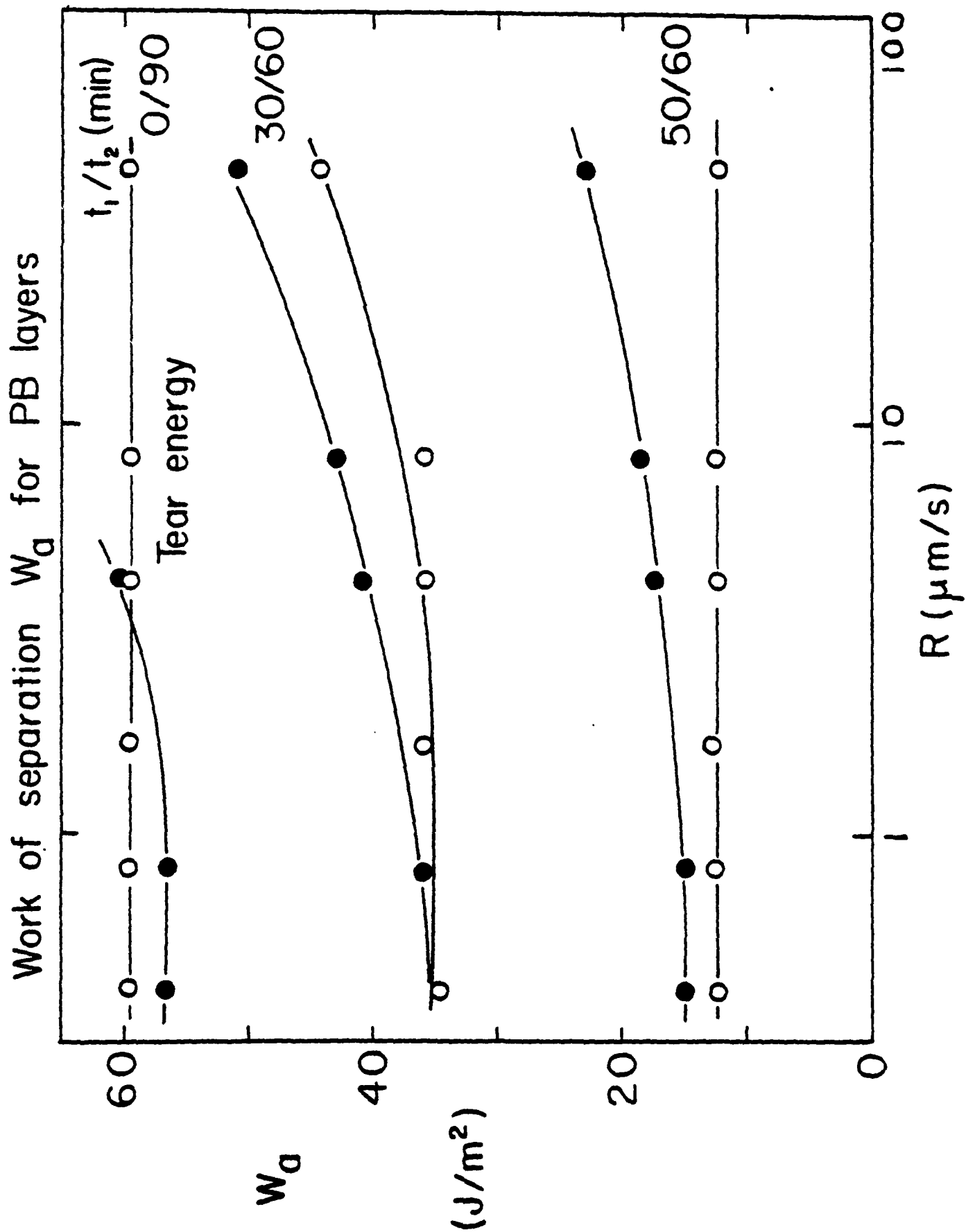0.075% DCP

0.2% DCP

W_o
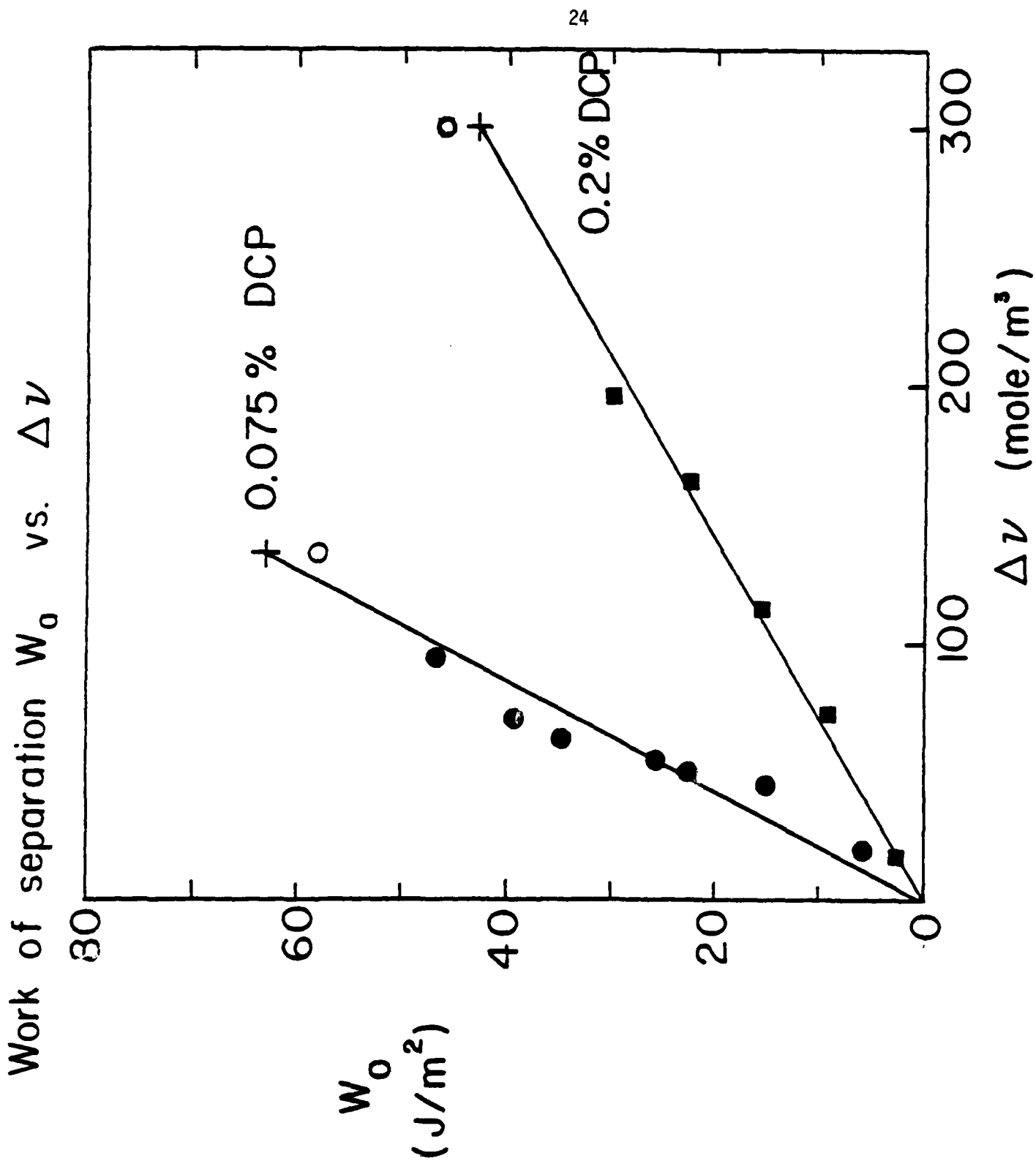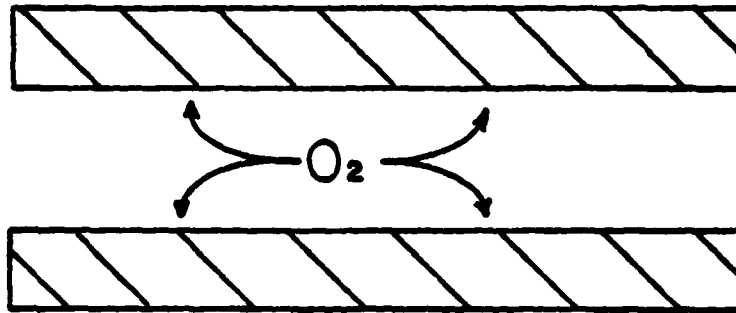(J/m^2)

$\Delta \nu$ (mole/m³)

FIGURE 6

Oxidative crosslinking of polybutadiene

Step 1

Exposed to air for time t (10sec—10days)
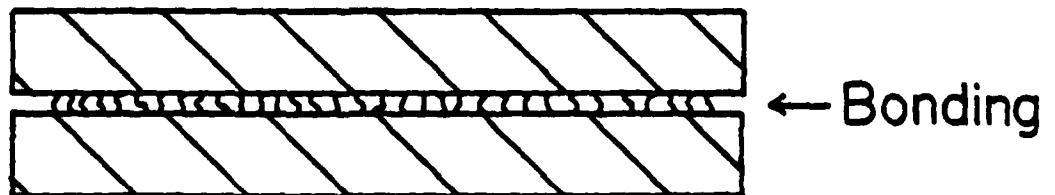

Step 2

Pressed together for 24 hours
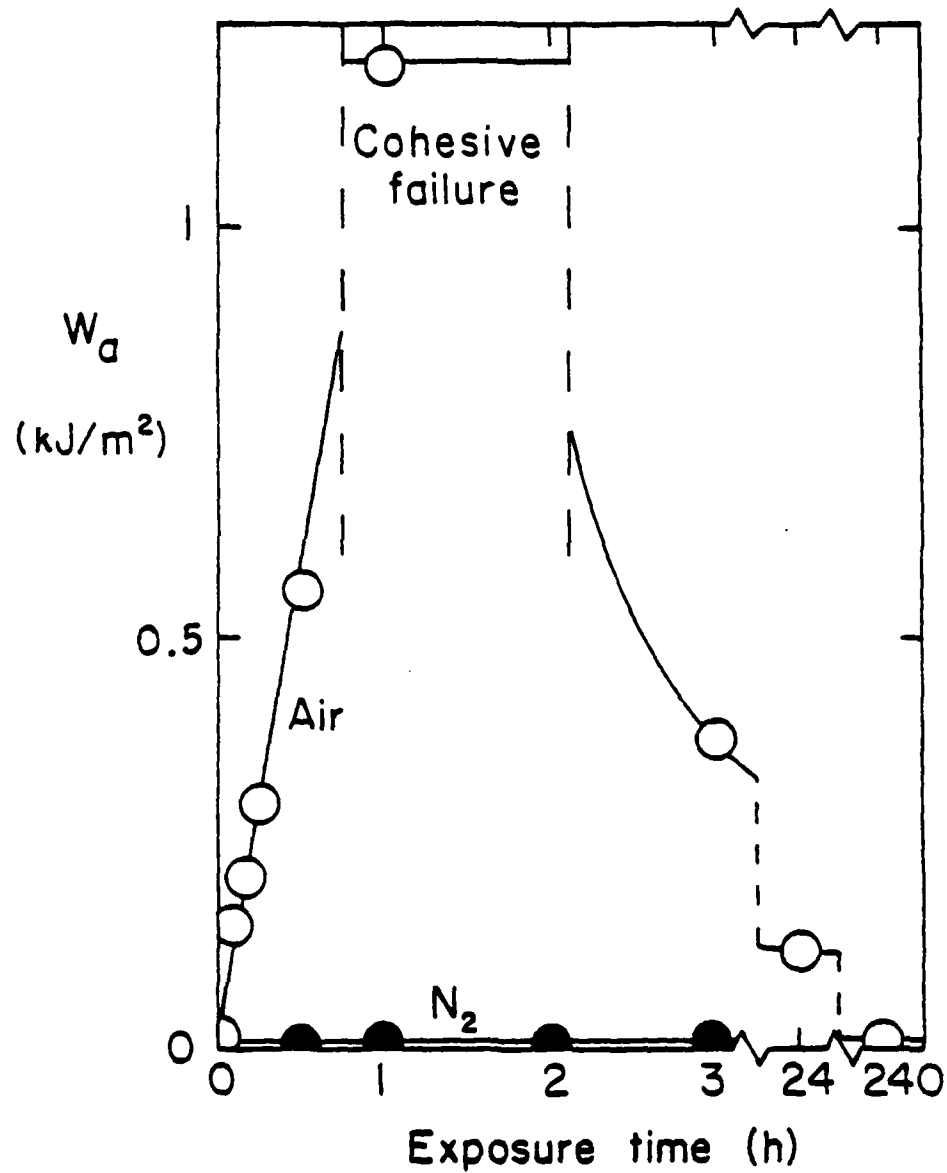

FIGURE 7

Work of separation W_a for PB layers

FIGURE 8

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